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[54] PROCESS OF BLACK CHROMIUM PLATING

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UNITED STATES PATENTS

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2,088,615	8/1937	Schlotter	204/51
2,354,756	8/1944	Keuffel et al.	204/51 UX
2,623,847	12/1952	Gilbert et al.	204/51
3,419,481	12/1968	Nelson	204/51

ABSTRACT: The process and the improved black chromium plating produced thereby comprising electroplating chromium from an aqueous bath containing hexavalent chromium, trivalent chromium and a lower aliphatic carboxylic acid such as acetic acid. The hexavalent chromium compound is present in a range equivalent to 150-425 grams per liter of chromic acid anhydride; the trivalent chromium is present in an amount 8-30 grams per liter; and the total carboxylic acid, in both acid and carboxylate form, is in the range of 170-350 grams per liter of acid. The electroplating is conducted at 60-85° F. and with a cathode current density of 75-1000 amperes per sq. ft. The trivalent chromium concentration given above not only permits reproducible lustrous black chromium plating but also greatly decreases the break-in period for the bath. A further addition of ferric ions of up to 25 grams per liter further decreases or completely eliminates the break-in period and also increases the maximum operating temperature of the plating bath to 105° F. When iron is utilized, the combined concentration of trivalent chromium and iron should not exceed 35 grams per liter.

PROCESS OF BLACK CHROMIUM PLATING

This application is a continuation-in-part of U.S. Application Ser. No. 610,035 filed Jan. 18, 1967, now abandoned.

This invention relates to a process for electrodepositing a black chromium plating, and the product produced by this process. More specifically, it relates to a process for electrodepositing on a suitable metallic substrate a black chromium plating from an aqueous electroplating bath comprising hexavalent chromium, trivalent chromium, and lower aliphatic acid, such as acetic acid.

Previous attempts have been made to produce black chromium plating from baths containing chromic anhydride and various other components such as sulfamic acid, fluosilicic acid, acetic acid, etc. The use of such electroplating solutions has found little commercial acceptance, because of various defects in the plating, such as insufficient deposit, lack of uniformity, insufficient depth of color, etc. Moreover, the processes using such baths have undesirable limitations in operating temperatures and current density ranges.

For example, U.S. Pat. No. 2,623,847 discloses for this purpose an aqueous solution of 275 parts chromic anhydride and 210 parts acetic acid using a current density of 15-1,000, preferably 40-90 amperes per square foot at a temperature of about 90°-150° F. The resultant film is reported to be dark gray to black. However, tests with this bath, using operating conditions recommended, show that the platings tend to have a gray to brown cast and the deposits lack uniformity over varying current density ranges. The depth of color obtained is likewise unsatisfactory. Various unsatisfactory results in luster, light reflectivity, and smoothness are also evident.

In accordance with the practice of this invention, black chrome platings are now obtained which have improved luster, good adherence, uniformity, good depth of color, and are adaptable to providing unique decorative effects. This new plating is applied to a conductive base metal, which is used as the cathode, by electroplating from an aqueous bath containing hexavalent chromium, trivalent chromium, and an unsubstituted lower aliphatic acid. For proper operating of the bath, it is essential that a substantial amount of trivalent chromium be present to produce the desired black deposit of uniform color and depth. If the hexavalent chromium is used without a substantial amount of trivalent chromium, the plating generally shows various shades of color and an insufficient depth of color.

The trivalent chromium can be added or prepared in situ by reduction of some of the hexavalent chromium also used. This reduction can be effected by the use of a reducing agent, such as methanol. Preferably, however, the trivalent chromium is added directly as chromic acetate, etc., and advantageously in solution form. By preparing the trivalent chromium in situ is meant to convey that the hexavalent chromium therein is reduced chemically prior to use in the bath. Some trivalent chromium can be produced by electrolyzing a bath. However, this process is extremely long requiring electrolysis on the order of two weeks or more before sufficient trivalent chromium can be formed in the bath so as to result in the practice of the instant invention. In fact, most, if not all, plating baths for electroplating black chromium deposits would possess an anode to cathode area ratio of at least 1 and preferentially a much higher ratio in order to operate efficiently and at these anode to cathode area ratios the buildup of trivalent chromium would reach equilibrium at a trivalent chromium concentration much less than the minimum necessary for the practice of the instant invention. This, too, would also require the periodic addition of trivalent chromium to maintain the appropriate concentration level in the bath. By the initial addition or reduction in situ of trivalent chromium, the conditioning of the bath prior to electrodeposition requires only a few hours and then bright lustrous black chromium deposits can be consistently obtained by maintaining the concentrations of the various addition agents in the ranges described with respect to the instant invention.

Acetic acid is preferred as the lower aliphatic acid although propionic, butyric, valeric acids, etc., can also be used.

The hexavalent chromium can be added in various forms, but is preferably added as chromic acid or its anhydride.

In view of the various reactions that can take place, it is generally desirable to express the composition of the electrolytic bath on the basis of the materials added. Moreover, since the resultant bath will have a substantial amount of acetate therein, it is generally desirable to state the total acetate content, including both acetates and acetic acid as the acetic acid equivalent.

The electrolytic bath suitable for the use in the process of this invention contains hexavalent chromium in an amount equivalent to 150-425 preferably about 250-350 grams per liter of chromic acid anhydride (CrO_3), 8-30, preferably 8-20 grams per liter of trivalent chromium, and the total acetate content, which is present either as acetate or acetic acid, should be equivalent to 170-350 preferably 200-300 grams per liter of acetic acid. For the purpose of this invention, the bath is operated at a temperature of 60°-85° F., preferably 65°-75° F., with a cathode current density of 75-1,000 amperes per square foot.

A preferred electrolytic bath for this invention contains the equivalent of 310 grams of chromium trioxide (CrO_3) per liter as the hexavalent chromium, 15 grams of trivalent chromium per liter, and a total acetate content equivalent to 300 grams of acetic acid per liter.

Excellent black deposits have also been secured from a bath containing the equivalent of 315 grams of CrO_3 per liter, 12.8 grams of trivalent chromium per liter and 287 grams of acetic acid per liter.

The trivalent chromium acetate can suitably be prepared by reducing a solution of chromic anhydride in aqueous acetic acid. A solution is prepared by dissolving 1,130 grams of chromic anhydride in an aqueous acetic acid solution containing about 2,330 grams of glacial acetic acid and a liter of water. This solution is warmed to about 175°-195° F. and there is then added slowly about 190 grams of methanol which has been diluted with an equal volume of water. Initially the solution has a red color, but upon reduction of the hexavalent chromium to trivalent chromium, the color turns green. When the evolution of gas stops, indicating no further reaction, about 380 grams of 35 percent hydrogen peroxide is slowly added with the temperature maintained at 130°-160° F. Here the hydrogen peroxide serves to further advance the reduction and avoids the use of a greater excess of methanol that would otherwise be required for the reduction. Water is added to compensate for evaporation losses. With this procedure, less than 5 percent of the chromium remains in the hexavalent state and the solution contains in the order of 120 grams per liter of trivalent chromium.

This chromic acetate solution and sufficient chromic anhydride and acetic acid to give the desired concentrations, are added to water to give the electroplating bath of desired concentration of hexavalent chromium, trivalent chromium, and acetate.

Since sulfate ions in the bath interfere with the production of a lustrous black deposit, a small amount of a barium compound, such as barium carbonate or barium acetate, is advantageously added to precipitate the sulfate. Generally, at least six grams per liter of the barium compound is sufficient for this purpose. After the various components have been added, diluted to the proper concentration and thoroughly mixed, the bath is conditioned by operating at ordinary plating conditions for a short period. This conditioning is effected with the application of 6-12 volts at 115° F. for at least 2 hours.

The conductive substrate on which the plating is to be deposited is generally stainless steel, steel, copper, or other suitable metal. Steel or zinc die castings which have been plated with copper or nickel are also suitable. Particularly suitable substrates for automotive and appliance use comprise steel which has been electroplated with one or more layers of nickel followed in some cases by a chromium electroplating from a typical bright chromium bath. Suitable substrates also

comprise zinc die-casts prepared by plating the die-cast with copper with one or more subsequent electroplatings of nickel, with or without an ultimate thin deposit of bright chromium. Plastic substrates can also be made conductive and used in the practice of this invention by the well known steps of electroless deposition of copper or nickel followed by electroplating with copper, nickel, or chromium.

The substrate to be plated is immersed in the bath and made the cathode in the electrical system. While anodes of various materials, such as stainless steel, carbon and lead can be employed, it has been found preferable to use an anode of ordinary carbon steel. Moreover, it has been found desirable to use a tank lined with a polyvinyl chloride or other suitable synthetic inert material. Preferably an exhaust system should be provided in association with the plating tank for carrying away fumes of acetic acid and chromic acid.

The baths are advantageously operated at a temperature of 60°-85 F., preferably about 75° F. Plating is effected satisfactorily at a current density as low as 75 amperes per square foot, and as high as 1,000 amperes per square foot. It has been found that in the process of this invention, extremely high current densities can be used successfully, that is, approximately 1,000 amperes per square foot, without the "burning" of the object being plated. With conventional plating solutions, the use of high current densities causes "burning" which results in numerous rejections of parts and accompanying high production costs. However, a cathode current density of about 150-400 amperes per square foot is preferred. Plating times as low as 30 seconds produce a deep black film of uniform color.

After the plating is completed, the article is removed from the bath, is given a conventional rinse, and while still wet, wiped with a soft absorbent material. If the substrate is bright, the resulting plate is glossy, but with a dull substrate the plating is less glossy.

For most efficient operation, it is desirable to have an anode area at least as great as but preferably considerably larger than the cathode area, for example as much as four times as great. By having the anode area larger than the cathode area, the anode current density is maintained at a relatively low value. A lower anodic current density helps to avoid a film coating on the anode which will increase the resistance of the system.

The components of the plating bath are replenished periodically by the addition of chromic anhydride, and acetic acid and if necessary, trivalent chromium. The first two are added in about the same proportion as in the original composition. Sufficiently accurate routine control for production is achieved by the use of a hydrometer to measure the specific gravity of the bath. If the plating bath becomes sluggish and shows poor covering power, the acetic acid content can be readjusted and water added to restore the bath to proper operation. In order to precipitate the sulfate introduced as additional chromic anhydride is added, or from the water, more barium compound should also be added as necessary.

As with all electroplating solutions, it is advisable to periodically determine by analysis the concentration of the CrO_3 , Cr^{+++} and acetic acid and make adjustments as indicated.

The plating produced according to the process of this invention is lustrous in appearance and extremely black in color. There is no need for subsequent polishing or buffing. Where it is desired to have less gloss in the plated surface, it is advantageous to use a matte surface for the final plating operation. It is believed that the improved results of this invention are attributed to the use of an electroplating bath having present a relatively high concentration of the acetate ion and of the trivalent chromium ion.

Various methods of practicing the invention are illustrated by the following examples. These examples are intended merely to illustrate the invention and not in any sense to limit the manner in which the invention can be practiced. The parts and percentages recited therein and all through the specification, unless specifically provided otherwise, are by weight.

EXAMPLE I

About 220 cc. of the trivalent chromium solution as prepared above so as to provide 25 grams of trivalent chromium is mixed with 310 grams of chromium trioxide (CrO_3) and an additional 213 parts of acetic acid. Approximately 6 grams of barium carbonate is added to precipitate any sulfate ions that may be present. The resultant solution is diluted with water to 1 liter and is used as the electrolyte in plating 12 small sheets of carbon steel 2 inches×2 inches square using each steel sheet as the cathode and an ordinary carbon steel electrode as the anode. The tank used to contain the electrolyte is lined with polyvinyl chloride. The plating is effected at a temperature of 75° F. and at a current density of 200 amperes per square foot. After plating for 5 minutes, a black chromium plating having excellent adhesion, luster, and uniformity and depth of color is obtained in each case, and there is uniformity and reproducibility between the respective platings.

EXAMPLE II

The procedure of example I is repeated except that the trivalent chromium is omitted, using 310 grams of chromic acid anhydride and 300 grams of acetic acid per liter of solution. A series of 12 platings, such as in example I, is performed. There are considerable variations in the plating in the amount deposited and in the depth of color, showing the importance of the trivalent chromium used in example I.

EXAMPLE III

The procedure of example I is repeated using in place of the sheets of carbon steel, corresponding sheets of stainless steel, copper and also steel and zinc castings which have been plated with copper and with nickel. In each case, similar good results are obtained as in example I.

EXAMPLE IV

The procedure of example I is repeated 3 times using individually in place of the acetic acid, equivalent amounts of propionic acid, butyric acid, and valeric acid respectively.

EXAMPLE V

The procedure of example I is repeated except that instead of preparing the trivalent chromium as described, an equivalent amount of chromic acetate is added directly. Similar results are obtained as in example I.

Likewise similar results are obtained when equivalent amounts of chromium propionate, chromium butyrate, and chromium valerate are used instead of the chromium acetate.

EXAMPLE VI

The procedure of example I is repeated, using 18 instead of 25 grams of trivalent chromium. Similar results are obtained as in example I.

Likewise similar results are obtained when the procedure of example I is repeated using 250 grams instead of the 310 grams of chromic anhydride and a total of approximately 220 grams of acetic acid instead of the approximately 265 grams of example I. Again excellent results are obtained, and also when 350 grams of chromic anhydride and approximately 310 grams of total acetic acid are used.

As a further improvement of the instant invention, ferric iron may be added to the electroplating bath of the instant invention. The ferric ion concentration added can be any concentration up to about 25 grams per liter. Preferably, the iron is present in a concentration of from 8-12 grams per liter. The addition of iron has a twofold effect on the instant black chromium electroplating process. First, it decreases the conditioning time required for such electroplating baths containing trivalent chromium from a few hours to a point where no conditioning is required and excellent lustrous black chromium deposits can be produced immediately upon making up the

bath. Secondly, the addition of iron to such baths allows the bath to operate at higher temperature levels. With iron, the operating temperature range is increased to 60°–105° F. When both trivalent chromium is present in the ranges previously discussed and iron is also included in the plating bath, the total concentration of trivalent chromium and ferric ion should be less than 35 grams per liter. The more iron that is present in the bath, the less trivalent chromium is required. In any event, however, there must be present at least about 8 grams per liter of trivalent chromium. Another correlation which exists in the practice of the instant black chromium electroplating process is that the greater the concentration of trivalent chromium and iron in the bath, the lower the concentration of acetic acid or other carboxylic acid addition agent is needed to obtain equivalent results. Thus, when the concentration of trivalent chromium and iron approach 35 grams per liter, the concentration of the carboxylic acid approaches the lower limits, that is, approximately 170–200 grams per liter.

The following examples illustrate the practice of the instant invention wherein iron is added along with trivalent chromium in the practice of the instant invention. In each of the following tables, the concentration of acetic acid, trivalent chromium and iron are given in grams per liter. The given concentrations of these addition agents were added to plating baths made up in 2 liter beakers equipped with steel cooling coils. The plating time was 3 minutes at 200 amperes per square foot while the bath temperature was maintained at 80° F. The bath used the following basic composition

CrO_3 —310 g./l.

BaCO_3 —5 g./l.

The trivalent chromium of each example below was added as the chromium acetate whereas the iron was added as ferric acetate.

Example No.	Acetic Acid	Cr^{+3}	Fe
VII	313	13	1.1
VIII	308	12.7	0.9
IX	296	14.4	1.3
X	266	12.5	3.8
XI	274	11.9	4.6
XII	209	12.4	
XIII	239	9.0	12
XIV	222	12.6	7.6
XV	264	8.8	7.1

All baths given in examples VII through XV produced bright lustrous black chromium electroplates on brass substrates which had previously been electroplated with a bright nickel surface without any conditioning of the electroplating bath except the bath of example VIII required a conditioning period of 15 minutes and the bath of example XII required a example period of 135 minutes. This conditioning was effected by the application of 9 volts at 115° F. for the stated periods.

The above examples VII–XI and XIII–XV were repeated utilizing a plating bath temperature of 105° F. with equivalent results.

Whereas, the iron in the above examples was added as the ferric acetate, other forms of iron can be used to supply the desired iron concentrations. Typically, the iron can be supplied in the form of acetate, oxylate and hydroxide or the like. Since chloride and sulfate ion are not desired in the instant plating bath, iron addition in this form should be avoided. However, should the sulfate be used for the addition, the sulfate ion could be removed by adding a sufficient amount of barium carbonate to completely precipitate out the sulfate ion.

While certain features of this invention have been described in detail with respect to various embodiments thereof, it will, of course, be apparent that other modifications can be made within the spirit and scope of this invention and it is not in-

tended to limit the invention to the exact details shown above except insofar as they are defined in the following claims. I claim:

1. The process of producing a deep black, corrosion-resistant, adherent chromium plating upon a conductive substrate, comprising the steps of:

a. making the said conductive substrate the cathode in an electroplating system in which the electroplating solution comprises an aqueous solution comprising a chromium compound having a hexavalent chromium content equivalent to 150–425 grams per liter of chromic acid anhydride, a trivalent chromium compound having a trivalent chromium content of 8–30 grams per liter and a lower aliphatic carboxylic acid present in a total amount equivalent to 170–350 grams per liter of acetic acid, said total amount of said carboxylic acid representing the amount present in both the acid and the carboxylate form, and

b. conducting the electroplating with said bath at a temperature of 60°–85° F. with a cathode current density of 75–1,000 amperes per square foot.

2. The process of claim 1 in which said carboxylic acid is acetic acid.

3. The process of claim 2 in which the substrate is steel.

4. The process of claim 3 in which the substrate is steel upon which a semibright nickel and subsequently a layer of bright nickel has been electrodeposited.

5. The process of claim 4 in which the substrate is steel on which there has been electrodeposited successive layers of semibright nickel, bright nickel, and bright chromium, respectively.

6. The process of claim 3 in which the substrate is steel upon which a bright nickel plating has been electrodeposited.

7. The process of claim 2 in which the substrate is die-cast zinc upon which there has been deposited copper and at least one layer of nickel.

8. The process of claim 7 in which the die-cast zinc is one on which there has been successively deposited a layer of copper, at least one layer of nickel, and a layer of bright chromium, respectively.

9. The process of claim 2 in which said hexavalent chromium content is equivalent to approximately 250–350 grams per liter of chromic acid anhydride, said trivalent chromium content is equivalent to approximately 8–20 grams per liter, and the total acetate content is equivalent to approximately 200–300 grams per liter of acetic acid.

10. The process of claim 2 in which said plating is conducted at a temperature of approximately 65°–75° F. and at an average cathode current density of about 150–400 amperes per square foot.

11. The process of claim 2 in which the substrate is a plastic material on which has been applied by electroless plating a layer of a metal selected from the class consisting of nickel and copper, at least one subsequent layer of an electrodeposited metal selected from the class consisting of copper and nickel, and a subsequent layer of bright chromium.

12. The process of producing a deep black, corrosion-resistant, adherent chromium plating upon a conductive substrate, comprising the steps of:

a. making the said conductive substrate the cathode in an electroplating system in which the electroplating solution comprises an aqueous solution comprising a chromium compound having a hexavalent chromium content equivalent to 150–425 grams per liter of chromic acid anhydride, a trivalent chromium compound having a trivalent chromium content of 8–30 grams per liter, iron at a concentration up to about 25 grams per liter, and a lower aliphatic carboxylic acid present in a total amount equivalent to 170–350 grams per liter of acetic acid, said total amount of said carboxylic acid representing the amount present in both the acid and the carboxylate form, said concentration of trivalent chromium and iron together not exceeding 35 grams per liter, and

b. conducting the electroplating with said bath at a temperature of 60°-105° F. with a cathode current density of 75-1,000 amperes per square foot.

13. The process of claim 12 in which said carboxylic acid is acetic acid.

14. The process of claim 13 in which said hexavalent chromium content is equivalent to approximately 250-350 grams per liter of chromic acid anhydride, said trivalent chromium content is equivalent to approximately 8-20 grams per liter, and the total acetate content is equivalent to approximately 200-300 grams per liter of acetic acid.

15. An electroplating bath for producing a deep black, corrosion resistant, adherent chromium plating upon a conductive substrate, comprising an acidic aqueous solution of a chromium compound having a hexavalent chromium content equivalent to 150-425 grams per liter of chromic acid anhydride, a trivalent chromium compound having a trivalent chromium content of 8-30 grams per liter and a lower aliphatic carboxylic acid present in a total amount equivalent to 170-350 grams per liter of acetic acid, said total amount of said carboxylic acid representing the amount present in both the acid and the carboxylate form.

16. The bath of claim 15 in which said carboxylic acid is acetic acid.

17. The bath of claim 16 in which said hexavalent chromium content is equivalent to approximately 250-350 grams per liter of chromic acid anhydride, said trivalent chromium con-

tent is equivalent to approximately 8-20 grams per liter, and the total acetate content is equivalent to approximately 200-300 grams per liter of acetic acid.

18. An electroplating bath for producing a deep black, corrosion-resistant, adherent chromium plating upon a conductive substrate, comprising an acidic aqueous solution of a chromium compound having a hexavalent chromium content equivalent to 150-425 grams per liter of chromic acid anhydride, a trivalent chromium compound having a trivalent chromium content of 8-30 grams per liter, iron at a concentration up to about 25 grams per liter, and a lower aliphatic carboxylic acid present in a total amount equivalent to 170-350 grams per liter of acetic acid, said total amount of said carboxylic acid representing the amount present in both the acid and the carboxylate form, and said concentration of trivalent chromium and iron together not exceeding 35 grams per liter.

19. The process of claim 18 in which said carboxylic acid is acetic acid.

20. The process of claim 19 in which said hexavalent chromium content is equivalent to approximately 250-350 grams per liter of chromic acid anhydride, said trivalent chromium content is equivalent to approximately 8-20 grams per liter, the total acetate content is equivalent to approximately 200-300 grams per liter of acetic acid and the iron content being from approximately 8-12 grams per liter.

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